#### (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

#### (19) World Intellectual Property Organization International Bureau



### 

(43) International Publication Date 4 November 2004 (04.11.2004)

PCT

# (10) International Publication Number

(51) International Patent Classification<sup>7</sup>:

WO 2004/095501 A2

H01J 37/00

(21) International Application Number:

PCT/US2004/011554

(22) International Filing Date:

15 April 2004 (15.04.2004)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

60/464,755

23 April 2003 (23.04.2003)

- (71) Applicant (for all designated States except US): H.C. STARCK INC.; 45 Industrial Place, Newton, MA 02461 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): DAILY, James [US/US]; 844 N. Wooded Lane, Marshall, MI 49068 (US). LEMON, Brad [US/US]; 15635 13 Mile Road, Battle Creek, MI 49014 (US). HIRT, Joseph [US/US]; 11 Parsons Court, Coldwater, MI 49036 (US). KUMAR, Prabhat [US/US]; 31 Pinewood Drive, Framingham, MA 01701 (US). GILLE, Gerhard [DE/DE]; Am Stollen 3, 38640 Goslar (DE).
- (74) Agents: AKORLI, Godfried, R. et al.; Bayer Chemicals Corporation, Patent Department, 100 Bayer Road, Pittsburgh, PA 15205-9741 (US).

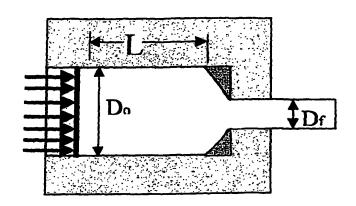
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### Published:

without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

#### (54) Title: MOLYBDENUM ALLOY X-RAY TARGETS HAVING UNIFORM GRAIN STRUCTURE



(57) Abstract: The invention relates to a process for making a cross-directionally worked molybdenum plate, the process comprising: (a) reducing ammonium molybdate and forming molybdenum metal powder; (b) consolidating a molybdenum component comprised of molybdenum metal powder and an alloying element to a first workpiece, the alloying element being selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof; (c) thermally treating the first workpiece and subjecting the workpiece to thermo-mechanical forces in a first direction, and thereby forming a second workpiece; (d) thermally treating the second workpiece and subjecting the second workpiece to thermo-mechanical forces in a second direction that

is different from the first direction; (e) subjecting the thermomechanically treated second workpiece to a recrystallization heat treatment step, and thereby forming a heat-treated cross-directionally worked workpiece; and (f) subjecting the heat-treated, cross-directionally worked workpiece to a slicing step or a machining step, and thereby forming the crossdirectionally worked molybdenum plate. The invention also relates to X-ray targets made from the process.

WO 2004/095501

PCT/US2004/011554

# MOLYBDENUM ALLOY X-RAY TARGETS HAVING UNIFORM GRAIN STRUCTURE

5

10

15

20

25

30

#### BACKGROUND OF THE INVENTION

X-ray producing devices are extremely valuable tools that are used in a wide variety of applications, both industrial and medical. For example, such equipment is commonly used in areas such as diagnostic and therapeutic radiology; semiconductor manufacture and fabrication; and materials analysis and testing.

While used in a number of different applications, the basic structure and operation of x-ray devices is similar. X-rays are produced when electrons are generated, accelerated to a high speed, and then stopped abruptly. Typically, this entire process takes place within a vacuum formed x-ray generating tube. An x-ray tube ordinarily includes three primary elements: a cathode assembly, which is the source of electrons; an anode, which is axially spaced apart from the cathode and oriented so as to receive electrons emitted by the cathode; and some mechanism for applying a high voltage for driving the electrons from the cathode to the anode. Usually, the cathode assembly is composed of a metallic cathode head having a cathode cup. Disposed within the cathode cup is a filament that, when heated via an electrical current, emits electrons.

The three x-ray tube elements are usually positioned within an evacuated glass tube and connected within an electrical circuit. The electrical circuit is connected so that the voltage generation element can apply a very high voltage (ranging from about ten thousand to in excess of hundreds of thousands of volts) between the anode and the cathode. This high voltage differential causes the electrons that are emitted from the cathode filament to accelerate at a very high velocity towards an x-ray "target" positioned on the anode in the form of a thin stream, or beam. The x-ray target includes a plate with a focal track. When the electrons strike

10

15

25

30



the target surface, the kinetic energy of the striking electron beam is converted to electromagnetic waves of very high frequency, i.e., x-rays. The resulting x-rays emanate from the anode target surface, and are then collimated through a window formed in the x-ray device for penetration into an object, such as an area of a patient's body.

Unfortunately, known processes for making plates have limitations that have prevented artisans from developing a simple effective process and for quickly effectively making plates useful in x-ray targets. A particularly limiting disadvantage of known single forging processes, for instance, is that such processes are wasteful and inefficient, making them costly and impractical to implement. Known processes make products have poor uniform grain size. Poor uniformity in grain size interferes with the performance of X-ray anodes. Also, known processes produce anodes having poor temperature properties.

For the foregoing reasons, there is a need to develop a process that produces x-ray targets having uniform properties.

For the foregoing reasons, there is a need to develop a process that produces x-ray targets having uniform properties.

#### 20 <u>SUMMARY OF THE INVENTION</u>

The invention relates to a process for making a cross-directionally worked molybdenum plate. The plate is preferably used in an X-ray target so that the plate functions as an anode. The process involves (a) reducing ammonium molybdate and forming molybdenum metal powder; (b) consolidating a molybdenum component made of molybdenum metal powder and an alloying element to a first workpiece, the alloying element being selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof; (c) thermally treating the first workpiece and subjecting the workpiece to thermo-mechanical forces in a first direction, and thereby forming a second workpiece; (d)

10

15

20

25

30

thermally treating the second workpiece and subjecting the second workpiece to thermo-mechanical forces in a second direction that is different from the first direction; (e) subjecting the thermomechanically treated second workpiece to a recrystallization heat treatment step, and thereby forming a heat-treated cross-directionally worked workpiece; and (f) subjecting the heat-treated, cross-directionally worked workpiece to a slicing step or a machining step, and thereby forming the cross-directionally worked molybdenum plate.

In one embodiment, the invention relates to a member made by such a process, in which the member includes a plate and a stem attached to the plate.

In one embodiment, the invention relates to a plate involving a cross-directionally worked molybdenum component selected from the group consisting of (i) a molybdenum component containing molybdenum and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof or (ii) a molybdenum component of molybdenum, niobium and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof or (iii) a molybdenum component of molybdenum, tungsten in an amount ranging from about 1 to about 30 wt.% and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof; in which the plate has a radial strength of at least about 60 ksi when the plate is exposed to a temperature of about 1600°C.

In another embodiment, the invention relates to an X-ray target: (a) a plate involving a cross-directionally worked molybdenum component selected from the group consisting of (i) a molybdenum component containing molybdenum and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and

10

20



combinations thereof or (ii) a molybdenum component including molybdenum, niobium and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof or (iii) a molybdenum component including molybdenum, tungsten in an amount ranging from about 1 to about 30 wt.% and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof; in which the plate has a radial strength of at least about 60 ksi when the plate is exposed to a temperature of about 1600°C; (b) a focal track located on a surface of the plate; and (c) a stem extending from the plate.

#### **DESCRIPTION OF THE FIGURES**

These and other features, aspects, and advantages of the present invention will become better understood with reference to the following description and appended claims, where:

- Fig. 1 is a schematic showing how a billet/ingot can be extruded in accordance to the invention;
- Figs. 2 (a) and 2 (b) are a schematic showing how the first workpiece can be upset forged in accordance to the invention;
  - Fig. 3(a) is a view of the second workpiece generated during the upset forging operation with removal of centering disk affected material at A;
- Fig. 3(b) is a view of the second workpiece formed from upset forging and a plate that can be sliced from the billet;
  - Fig. 4 is a side view showing a workpiece being subjected to hammer forging;
  - Fig. 5 shows the second workpiece formed from a workpiece that is subjected to hammer forging; and

10

15

20

25

30

- 5 -

Fig. 6 is a side view of a stem that can be attached to the plate made in accordance to the invention.

#### **DESCRIPTION OF THE INVENTION**

The cross-directionally worked molybdenum plate is generally made by a process that (a) reduces ammonium molybdate and forming molybdenum metal powder; (b) consolidates a molybdenum component made of molybdenum metal powder and an alloying element to a first workpiece, the alloying element being selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof; (c) thermally treats the first workpiece and subjecting the workpiece to thermo-mechanical forces in a first direction, and thereby forming a second workpiece; (d) thermally treats the second workpiece and subjecting the second workpiece to thermo-mechanical forces in a second direction that is different from the first direction; (e) subjects the thermomechanically treated second workpiece to a recrystallization heat treatment step, and thereby forming a heat-treated cross-directionally worked workpiece; and (f) subjects the heat-treated, cross-directionally worked workpiece to a slicing step or a machining step, and thereby forms the cross-directionally worked molybdenum plate.

The molybdenum metal powder is made by reducing ammonium molybdate by any suitable process. Generally, this is done through a conventional hydrogen reduction process. The process consolidates a molybdenum component including molybdenum metal powder and an alloying element to a first workpiece. In one embodiment, the molybdenum component is consolidated into the first workpiece by a powder metallurgical technique. Such a process generally involves the steps of cold isostatic pressing of the molybdenum metal powder and any alloying components into a "green" preform of the first workpiece. In another embodiment, the molybdenum component is consolidated into the

10

15

20

25

30



first workpiece by a melt casting technique. Such a process may involve vacuum arc casting, ebeam melting, or plasma arc casting of an ingot. The alloying element is generally selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof. In one embodiment, the first workpiece further includes niobium in an amount that is less than about 3 wt.%, preferably from about 1 wt % to about 3 wt.%. In another embodiment, the alloying element is present in an amount that is about 1.2 wt. %, or less. In another embodiment, the alloying element is present in an amount ranging from about 1 wt.% to about 1.5 wt.%. In another embodiment, the first workpiece further includes tungsten in an amount ranging from about 1 to about 30 wt.%.

The first workpiece is thermally treated and subjected to thermomechanical forces in a first direction, so that a second workpiece forms. The thermal treatment of the first workpiece is generally done at a temperature that is at least about 2100°F (about 1148°C) and preferably from about 2500°F (about 1371°C) to about 3000 °F (1648°C).

The thermally treated first workpiece is subjected to any thermomechanical treatment, which when practiced in accordance to the invention, produces a plate that is useful in an X-ray target. In one embodiment, the first workpiece is a billet or an ingot and the first workpiece is thermo-mechanically treated by extruding the billet or the ingot to a ratio of reduction (D<sub>o</sub>:D<sub>f</sub>) in a cross-sectional area ranging from about 3:1 through about 4:1. More particularly, referring to Fig. 1, the billet/ingot is extruded along length "L" to a suitable ratio of reduction (D<sub>o</sub>:D<sub>f</sub>). The billet length can be vary and preferably is from about 14" (about 36 cm) to about 32" (about 82 cm).

The second workpiece is then thermally treated and subjected to thermo-mechanical forces in a second direction that is different from the first direction. In one embodiment, the second workpiece is subjected to upset forging. The thermal treatment of the first workpiece is generally

10

15

20

25

30

done at a temperature that is at least about 2100°F (about 1148°C) and preferably from about 2500°F (about 1371°C) to about 3000 °F (1648°C).

The thermally treated second workpiece is subjected to any thermomechanical treatment, which when practiced in accordance to the invention, produces a plate that is useful in an X-ray target. In one embodiment, the second workpiece is upset forged by a closed die forging process with a closed die that is dimensioned to form a plate. In another embodiment, the second workpiece is upset forged by an open die (pancake) forging process with an open die that is dimensioned to form a plate. In another embodiment, the closed die is further dimensioned to include a mold for a stem (shown in Fig. 6) so that the plate formed by the process further includes a stem. As such, the invention encompasses a member made by the process of the invention, in which the member has a plate and a stem attached to the plate.

Referring to Figs. 2(a) and 2(b), Fig. 2(a) shows the first workpiece (10) at the start of the upset forging process in which the workpiece is placed in the press liner (12), between centering disks (14,16) and within an extrusion liner (19), such the moving centering disk (14) applies a main ram tonnage (18) against the stationary centering disk (16).

Fig. 2(b) depicts the end of the forming process in which the workpiece (10) has been subjected to thermo-mechanical forces thereby forming a forged workpiece (or forged billet (20)).

In another embodiment, as shown in Figs. 4 and 5, the second workpiece is subjected to hammer-forging instead of upset forging. Fig. 4 shows a workpiece being subjected to hammer forging, and Fig. 5 shows the second workpiece formed from the first workpiece. In this embodiment, the ratio of  $D_{\rm o}$  cross-sectional area to  $D_{\rm f}$  cross-sectional area preferably ranges from 1:2.0 to 1:2.8

The thermo-mechanically treated second workpiece is subjected to a recrystallization heat treatment step to form a fully annealed, cross-

10

15

20

25

30



directionally worked workpiece. This is generally done by through conventional heat treatment methods.

The heat treatment is generally done at a temperature that is at least about 2100°F (about 1148°C) and preferably from about 2500°F (about 1371°C) to about 3000 °F (1648°C).

The heat-treated, cross-directionally worked workpiece is then subjected to a slicing step or a machining step, and thereby the cross-directionally worked molybdenum plate forms. The material that does not form the billet during upset forging (the "affected material") is removed by the centering disks (CD), as shown in Fig 3(a) and 4.A plate can be sliced from the billet per the orientation shown in the Fig. 3(b) Advantageously, the entire billet is useful for making plates.

The plate made by the process of the invention has any suitable dimension that enables the plate to be used in a sputtering target. In one preferred embodiment, the plate has a diameter ranging from about 6" (about 15 cm) to about 14" (about 36 cm) and a thickness/height ranging from about 0.5" (about 1 cm) to about 2" (about 5 cm). In another embodiment, the plate has a diameter ranging from about 1" (about 2.54 cm) to about 14" (about 36 cm) and a thickness/ height ranging from about 1/4" (about 0.6 cm) to about 7" (about 18 cm).

Advantageously, the plate made in accordance to the invention has high temperature properties. In one embodiment, the plate has a radial strength of at least about 60 ksi when the plate is exposed to a temperature of about 1600°C. When the alloying element includes lanthanum oxide, the plate made by the process of the invention has improved creep resistance, as compared to a plate made without lanthanum oxide. In one embodiment the plate further includes a stem.

As such, in a preferred embodiment of the invention, the invention provides a plate having a cross-directionally worked molybdenum component selected from the group consisting of (i) a molybdenum

10

15

20

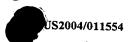
25

component containing molybdenum and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof or (ii) a molybdenum component including molybdenum, niobium and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof or (iii) a molybdenum component made of molybdenum, tungsten in an amount ranging from about 1 to about 30 wt.% and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof; in which the plate has a radial strength of at least about 60 ksi when the plate is exposed to a temperature of about 1600°C.

In one embodiment, the stem also includes a cross-directionally worked molybdenum component selected from the group consisting of (i) a molybdenum component containing molybdenum and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof or (ii) a molybdenum component involving molybdenum, niobium and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof or (iii) a molybdenum component including molybdenum, tungsten in an amount ranging from about 1 to about 30 wt.% and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof, in which the stem also has a strength of at least about 60 ksi when the stem is exposed to a temperature of about 1600°C.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

15



#### WHAT IS CLAIMED IS:

- 1. A process for making a cross-directionally worked molybdenum plate, the process comprising:
- (a) reducing ammonium molybdate and forming molybdenum metal 5 powder;
  - (b) consolidating a molybdenum component comprised of molybdenum metal powder and an alloying element to a first workpiece, the alloying element being selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof;
  - (c) thermally treating the first workpiece and subjecting the workpiece to thermo-mechanical forces in a first direction, and thereby forming a second workpiece;
  - (d) thermally treating the second workpiece and subjecting the second workpiece to thermo-mechanical forces in a second direction that is different from the first direction;
  - (e) subjecting the thermomechanically treated second workpiece to a recrystallization heat treatment step, and thereby forming a heat-treated crossdirectionally worked workpiece; and
- (f) subjecting the heat-treated, cross-directionally worked
   workpiece to a slicing step or a machining step, and thereby forming the cross-directionally worked molybdenum plate.
  - 2. The process of Claim 1, wherein the first workpiece further comprises niobium in an amount that is less than about 3 wt.%.
  - The process of Claim 1, wherein the first workpiece further comprises tungsten in an amount ranging from about 1 to about 30 wt.%.
    - 4. The process of Claim 1, wherein the molybdenum component is consolidated into the first workpiece by a powder metallurgical technique.

25

- 5. The process of Claim 1, wherein the molybdenum component is consolidated into the first workpiece by an arc casting technique.
- 6. The process of Claim 5, wherein the arc casting technique is a vacuum arc casting technique.
  - 7. The process of Claim 1, wherein the first workpiece is a billet or an ingot and the first workpiece is thermo-mechanically treated by extruding the billet or the ingot to a ratio of reduction (D<sub>o</sub>:D<sub>f</sub>) in a cross-sectional area ranging from about 3:1 through about 4:1.
- 10 8. The process of Claim 1, wherein in step (d), the second workpiece is subjected to upset forging.
  - 9. The process of Claim 8, wherein second workpiece is upset forged by a closed die forging process with a closed die that is dimensioned to form a plate.
- 15 10. The process of Claim 8, wherein second workpiece is upset forged by an open die forging process with an open die that is dimensioned to form a plate.
  - 11. The process of Claim 9, wherein in step (d), the closed die is further dimensioned to include a mold for a stem so that the plate formed by the process in step (e) further comprises a stem.
  - 12. A member made by the process of Claim 11, wherein the member comprises a plate and a stem attached to the plate.
  - 13. A plate made from the process of Claim 1, wherein the plate is a cross-directionally worked plate having a uniform grain structure.
  - 14. The process of Claim 1, wherein the alloying element is present in an amount that is about 1.2 wt. %, or less.
  - 15. The process of Claim 1, wherein the alloying element is present in an amount ranging from about 1 wt.% to about 1.5 wt.%.

25

20



- 16. The process of Claim 1, wherein the plate has a diameter ranging from about 1" to about 14" and a thickness/height ranging from about 1/4" to about 7".
- 17. The process of Claim 1, wherein the plate made by the 5 process has a radial strength of at least about 60 ksi when the plate is exposed to a temperature of about 1600°C.
  - 18. The process of Claim 1, wherein the alloying element comprises lanthanum oxide, and the plate made by the process has improved creep resistance, as compared to a plate made without lanthanum oxide.
- 19. A plate comprising a cross-directionally worked molybdenum component selected from the group consisting of (i) a molybdenum component containing molybdenum and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof or (ii) a molybdenum component 15 comprising molybdenum, niobium and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof or (iii) a molybdenum component comprising molybdenum, tungsten in an amount ranging from about 1 to about 30 wt.% and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof;

wherein the plate has a radial strength of at least about 60 ksi when the plate is exposed to a temperature of about 1600°C.

- 25 The plate of Claim 19, wherein the plate further comprises a 20. stem.
  - 21. An X-ray target comprising:
- a plate comprising a cross-directionally worked molybdenum (a) component selected from the group consisting of (i) a molybdenum component containing molybdenum and an alloying element selected from 30

the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof or (ii) a molybdenum component comprising molybdenum, niobium and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof or (iii) a molybdenum component comprising molybdenum, tungsten in an amount ranging from about 1 to about 30 wt.% and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof;

wherein the plate has a radial strength of at least about 60 ksi when the plate is exposed to a temperature of about 1600°C;

- (b) a focal track located on a surface of the plate; and
- (c) a stem extending from the plate.
- 22. The target of Claim 21, wherein the stem comprises a 15 worked molybdenum component selected from the group consisting of (i) a molybdenum component containing molybdenum and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof or (ii) a molybdenum component comprising molybdenum, niobium and an alloying element 20 selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and combinations thereof or (iii) a molybdenum component comprising molybdenum, tungsten in an amount ranging from about 1 to about 30 wt.% and an alloying element selected from the group consisting of titanium, zirconium, hafnium, carbon, lanthanum oxide, and 25 combinations thereof.

wherein the stem also has a strength of at least about 60 ksi when the stem is exposed to a temperature of about 1600°C.



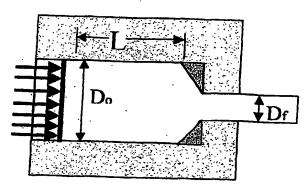


Fig. 1

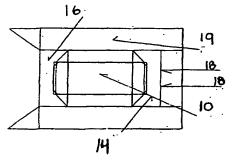


Fig. 2(a)

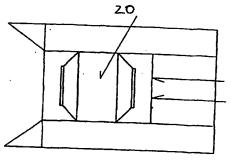


Fig. 2(b)

WO 2004/095501

PCT/US2004/011554

2/3

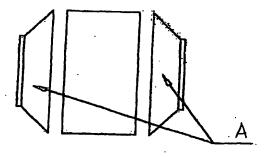


Fig. 3(a)

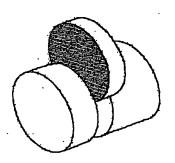


Fig. 3(b)

3/3

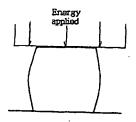


Fig. 4

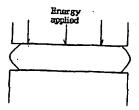


Fig. 5

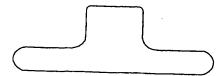


Fig. 6

Internation No PCT/US2004/011554

ation) DOCUMENTS CONSIDERED TO BE BELLEVANT	PCT/US2004/011554		
manages, militare appropriate, of the relevant passages	Relevant to claim No.		
WO 02/070765 A (KUMAR PRABHAT; JEPSON PETER R (US); STARCK H C INC (US); UHLENHUT HEN)	1-10, 13-18		
abstract page 1, paragraph 2 page 5, paragraph 15 — paragraph 16 page 7, paragraph 26 — page 8, paragraph	19–22		
page 11, paragraph 39 - page 12, paragraph 42			
claims 1,8,9,11-13,19,23,24; figures	}		
US 5 868 876 A (BIANCO ROBERT ET AL) 9 February 1999 (1999-02-09)	19		
column 1, line 14 - column 2, line 4 column 2, line 27 - column 3, line 15 column 3, line 49 - column 4, line 60 claims; figures	1-10, 13-18		
GB 938 546 A (DU PONT) 2 October 1963 (1963-10-02) page 1, line 11 - line 22 page 2, line 1 - line 41 page 3, line 8 page 4, line 62 - line 78 page 5, line 84 - line 104 page 6, line 25 - line 83 page 7, line 113 - page 8, line 9 claims; figures; example 18	1-10, 13-18		
US 2001/001401 A1 (SEGAL VLADIMIR) 24 May 2001 (2001-05-24) paragraph '0001! paragraph '0014! paragraph '0025! - paragraph '0026! paragraph '0031! - paragraph '0038! paragraph '0041! paragraph '0052! - paragraph '0059! claim 1; figures	1-10, 13-16 19-22		
US 2003/052000 A1 (FERRASSE STEPHANE AL) 20 March 2003 (2003-03-20) abstract figures paragraph '0001! paragraph '0004! - paragraph '0012! paragraph '0038! paragraph '0043! - paragraph '0044! paragraph '0047! - paragraph '0069! paragraph '0090! - paragraph '0091! paragraph '0097! - paragraph '0099! claims	1-7, 13-17 19-22		
	WO 02/070765 A (KUMAR PRABHAT; JEPSON PETER R (US); STARCK H C INC (US); UHLENHUT HEN)  12 September 2002 (2002-09-12) abstract page 1, paragraph 2 page 5, paragraph 15 - paragraph 16 page 7, paragraph 26 - page 8, paragraph 29 page 11, paragraph 39 - page 12, paragraph 42 claims 1,8,9,11-13,19,23,24; figures  US 5 868 876 A (BIANCO ROBERT ET AL) 9 February 1999 (1999-02-09) abstract  column 1, line 14 - column 2, line 4 column 2, line 27 - column 3, line 15 column 3, line 49 - column 4, line 60 claims; figures  GB 938 546 A (DU PONT) 2 October 1963 (1963-10-02) page 1, line 11 - line 22 page 2, line 1 - line 41 page 3, line 8 page 4, line 62 - line 78 page 5, line 84 - line 104 page 6, line 25 - line 83 page 7, line 113 - page 8, line 9 claims; figures; example 18  US 2001/001401 A1 (SEGAL VLADIMIR) 24 May 2001 (2001-05-24) paragraph '0001! paragraph '001! paragraph '001! paragraph '005! - paragraph '0059! claim 1; figures  US 2003/052000 A1 (FERRASSE STEPHANE ET AL) 20 March 2003 (2003-03-20) abstract figures paragraph '0004! paragraph '0001! paragraph '0004! paragraph '0009! paragraph '0099! paragraph '0099! paragraph '0099! paragraph '0099!		

PCT 04/011554

: (Continu	ation) DOCUMENTS CORED TO BE RELEVANT	PCT/	4/011554
Category °	Citation of document, with indication, where appropriate, of the relevant passages		Relevant to claim No.
<del>.</del>	US 2001/036249 A1 (BENZ MARK GILBERT ET AL) 1 November 2001 (2001-11-01)		1-22
١	the whole document  EP 0 055 828 A (GEN ELECTRIC) 14 July 1982 (1982-07-14) the whole document		1–22
	US 2001/014568 A1 (ITOH MASAYUKI ET AL) 16 August 2001 (2001-08-16) the whole document		19,21
,х	US 6 707 883 B1 (BALASUBRAMANIAN SRIHARI ET AL) 16 March 2004 (2004-03-16)		19-22
	abstract column 1, line 7 - line 11 column 2, line 16 - line 52 column 3, line 15 - column 4, line 39 column 5, line 10 - column 6, line 8 claims; figures		1–18
, А	WO 2004/022801 A (OSRAM SYLVANIA INC; WINNICKA MARIA B (US)) 18 March 2004 (2004-03-18) the whole document		1-18
	•		

International application No. PCT/US2004/011554

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)
This international Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
Claims Nos.:     because they relate to subject matter not required to be searched by this Authority, namely:
2. X Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  See FURTHER INFORMATION sheet PCT/ISA/210
3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)
This international Searching Authority found multiple inventions in this international application, as follows:
As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
As only some of the required additional search fees were timely paid by the applicant, this international Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the Invention first mentioned in the claims; it is covered by claims Nos.:
Remark on Protest  The additional search fees were accompanied by the applicant's protest.  No protest accompanied the payment of additional search fees.

#### FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.:

Present claims 17 and 19 to 22 relate to a method or product, respectively, defined (inter alia) by reference to the following parameter:

"radial" strength

The use of this parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameter the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to: molybdenum components having high-strength and creep-resistance at elevated temperatures.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.



Information on patent family members

International Application No PCT/US2004/011554

	Nat1 1		PCT/US2004/011554			2004/011554	
cite	Patent document ed in search report		Publication date		Patent family member(s)		Publication date
US	4077811	Α	07-03-1978	AT	818477	7 A	15-09-1980
				DE	2751623	λ Δ1	07-09-1980
			*	DK	497377		07-09-1978
				FR	2382287		02-09-1978
				GB			29-09-1978
					1557497		12-12-1979
				JP	53106615	A	16-09-1978
WO	02070765	Α	12-09-2002	BR	0207384		10-02-2004
				CA	2438819	A1	12-09-2002
				CZ	20032246	A3	17-03-2004
				EΡ	1366203		03-12-2003
				ΗÜ	0303269		28-01-2004
				JP	2004526863		
				NO	2004526863		02-09-2004
				NZ			26-09-2003
					527628		30-07-2004
				WO	02070765	AI	12-09-2002
				US 	2002112789	A1	22-08-2002
US 	5868876	Α	09-02-1999	NONE			
GB	938546	A	02-10-1963	DE	1286303	В	02-01-1969
US	2001001401	A1	24-05-2001	EP	1027463	Δ1	16-08-2000
	· - · - •			ĴΡ	2003532791	T T	
				WO		-	05-11-2003
				WG US	9902743		21-01-1999
					2003052000		20-03-2003
			·	US	6238494	 RT	29-05-2001
US	2003052000	A1	20-03-2003	US	2001001401		24-05-2001
				AU	6530901		17-12-2001
				WO	0194660		13-12-2001
				EP	1027463		16-08-2000
				JΡ	2003532791		05-11-2003
				WO	9902743		21-01-1999
				US	6238494		29-05-2001
				TW	397722		11-07-2000
							11-0/-2000
JS	2001036249	A1	01-11-2001	US	6256376	B1	03-07-2001
				AT	20942000		15-10-2004
ΞP	0055828	A	14-07-1982	EP	0055828	 Δ2	14-07-1982
				ĴΡ	57136752		23-08-1982
JS	2001014568	A1	16-08-2001	JP	3053345	P2	
- •		L/T	10 00-5001		3052240		12-06-2000
				JP	11312484		09-11-1999
				AT	231283		15-02-2003
				DE	69904865		20-02-2003
				DE	69904865		22-05-2003
				EP	0939427		01-09-1999
				US	6233311	B1	15-05-2001
JS	6707883	B1	16-03-2004	NONE			
٩U	2004022801	Α	18-03-2004	WO	2004022801	Δ1	18-03-2004

# This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

#### **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

BLACK BORDERS

IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

FADED TEXT OR DRAWING

BLURRED OR ILLEGIBLE TEXT OR DRAWING

SKEWED/SLANTED IMAGES

COLOR OR BLACK AND WHITE PHOTOGRAPHS

GRAY SCALE DOCUMENTS

LINES OR MARKS ON ORIGINAL DOCUMENT

REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

#### IMAGES ARE BEST AVAILABLE COPY.

□ OTHER: \_\_\_\_\_

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.